

## **CHARACTERISATION AND QUANTIFICATION OF DEPOSITS FROM THERMALLY STRESSED AVIATION FUELS**

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### **1. INTRODUCTION**

Deposits generated during thermal stressing of jet fuels in the JFTOT (Jet Fuel Thermal Oxidation Tester) hold a great deal of potential information about the mechanism and chemistry of fuel degradation, providing a suitable technique can be found for "unlocking" the data. Previous work at the BP Research Centre at Sunbury-on-Thames (RCS) using Auger Electron Spectroscopy has shown that magnesium (present in the tube alloy) will segregate at the tube surface and inhibit carbon deposition (1). The aims of recent work are to investigate further the causes and mechanisms of deposition, both in terms of chemical species and physical parameters.

JFTOT tube deposits have been examined by Scanning Electron Microscopy/Energy Dispersive Analysis of X-rays (SEM/EDX). This non-destructive technique enables a "profile" of the relative abundance of different elements present in the deposit along the tube length to be drawn. Further chemical characterisation of deposits has been made using Laser Ionisation Mass Analysis (LIMA); again, analysis has been performed along the length and through the depth of the deposit, providing information on deposit profiles in relation to tube temperature. It is now possible to obtain reproducible and reliable information about deposition levels enabling the influence of different factors such as temperature, time and fuel composition to be studied.

Much effort has been devoted during the past decade to characterisation of JFTOT tube deposits with less attention being given to the formation of particulate material during thermal stressing of fuels. It is believed that these could have as equally deleterious effects in aircraft fuel systems as surface layer deposits. Specific fuels are known to produce sufficient particulate material during normal JFTOT tests to give a measurable pressure differential across the standard JFTOT 17  $\mu\text{m}$  Dutch weave test filter. To study the formation of filterable deposits, an Alcor HLPS (Hot Liquid Process Simulator) has been modified at RCS to incorporate a 0.45  $\mu\text{m}$  Millipore membrane downstream of the heater tube test section, as a direct replacement for the standard filter. Filterable particulate deposits are collected during tests and characterised in terms of total mass and chemical composition.

Use of LIMA and SEM/EDX to characterise deposits generated in the JFTOT and the modified HLPS apparatus is described in this paper, with particular reference to the influence of fuel composition and test operating conditions on tube deposition and filterable deposit formation.

### **2. APPLICATION OF SEM/EDX TO JFTOT TUBE DEPOSIT ANALYSIS**

In SEM/EDX, bombardment of the deposit with a low energy probe (3.0kv) enables X-rays to be generated from the individual elements present at the point of analysis. This energy is sufficient to ensure that an aluminium signal from the tube itself is seen whilst maximising the surface sensitivity. Thus a ratio of the particular element under investigation to the aluminium can be given. As the thickness of the deposit varies, the response due to both carbon and aluminium will alter respectively. It is therefore not possible to give an absolute value to the carbon content, but by quoting it as a ratio to the aluminium, a comparative value is obtained. Repetitive analysis at points along the deposit length enables a profile of C/Al values with tube position to be plotted. Calibration of the peak areas, using

carbon films of known thickness would allow at least semi-quantitative measurement of deposit thickness. Owing to the varying response of the technique to different elements, it is not possible to establish relationships between different elements in one deposit, only to compare the abundance of any one element from deposit to deposit.

Typical profiles are given (Fig 1) with the profile obtained from an unused tube included for comparison. Uniformity of the deposit was checked by determining the profile on two sides of the tube. A small difference was observed, but this was not thought to be significant.

From the profile obtained from a typical JFTOT deposit, the carbon concentration is seen to be symmetrical about a point which occurs downstream of the maximum tube temperature (39mm). There is a substantial increase in the amount of deposition after the maximum tube temperature. Where TDR traces show "splitting" of peaks, SEM/EDX has shown the deposit to consist of a single gaussian distribution envelope mainly of carbon. This throws some doubt on the validity of the TDR for tubes with thicker deposits.

#### 2.1 Relationship between deposition and tube assessment

The relationship between visual ratings, TDR values and SEM/EDX traces is shown (Figs 2,3). There is good agreement, although SEM/EDX can identify trace levels of degradation carbon on a tube that has been given a visual rating of 1 and a TDR rating of zero. It is clear that the sensitivity of any assessment technique must be taken into account when defining the breakpoint of fuel as the temperature at which "onset of deposition" occurs.

#### 2.2 Prediction of fuel breakpoint

The deposit C/Al ratio at any point in the profile can be plotted against the corresponding tube temperature; two values for each temperature are obtained, one upstream and one downstream of the maximum tube temperature (Fig 4). For a given fuel run at different temperatures in JFTOT tests, the C/Al ratios at equivalent tube temperatures on the upstream side of the maximum tube temperature show good agreement (Fig 5). This suggests that the thickness of deposits generated during JFTOT tests may be constant at a specific tube temperature for a given fuel. Thus with knowledge of carbon thickness associated with a visual rating of 3, it may be possible to estimate the breakpoint temperature of a fuel from the SEM/EDX profile generated from a single JFTOT test at a temperature higher than the breakpoint. This procedure may find applications for research purposes.

#### 2.3 Kinetics of deposition

Maximum C/Al ratios obtained for one fuel at a constant temperature are plotted against test duration in Fig 6. The extent to which the non-linear response of the SEM/EDX to deposits of varying thickness affects these results is not known. However, the extended "induction period" observed implies a genuine change in mechanism, with deposition perhaps being governed by either a catalytic reaction with the tube surface or by an adherence effect. Others have also noticed this so-called "induction period" before the onset of deposition (2). The significance of this "induction period" with respect to aircraft fuel system operation needs to be established.

#### 2.4 Role of metals and MDA (Metal Deactivator Additive)

The presence of metals in fuel causes a reduction in thermal stability, although it is not known whether the metal plays an integral part in deposition or acts only in a catalytic capacity. Addition of MDA generally produces an apparent increase in thermal stability as perceived by the JFTOT. The mechanism for this "improvement" is not understood clearly and may be ascribed either to a bulk fuel reaction or to a "passivation" of the tube surface. In order to address some of these aspects, experiments were carried out using one fuel with differing levels of metals, MDA and metal/MDA; results are shown in Table 1.

It is shown (Table 1, Fig 7) that copper had a deleterious effect on the thermal stability of the fuel, with an increase in carbon deposition with increasing levels of copper. Interestingly, copper was observed in the deposit and was also seen to increase as fuel copper levels were increased (Fig 8). When MDA was added, the thermal stability was seen to improve over and above that of the base fuel. This time, however, there was no evidence for copper in the deposit, indicating that the metal chelate plays no part in deposition. This would imply that the free copper reacts with species in the fuel to cause deposition, but will preferentially bind to the MDA. It is apparent that the MDA performs its accepted role well in metal chelation, and also appears to have some other additional effect on JFTOT results as yet not fully understood. Tubes run with dodecane doped with copper showed that in the absence of a deposit no copper was detected on the tube surface.

Addition of iron to the fuel was seen to promote deposition to a much greater extent, but, in contrast to the copper, iron was not found to be present in the deposit. Although MDA was found to negate the effect of the iron, the additive was not as efficient as with the copper at improving JFTOT breakpoint.

Iron appears to play a catalytic role in deposit formation. Although chelation with MDA reduces its activity, it may be that some limited catalysis can still occur even in the chelated form or that the chelate is not thermodynamically stable at higher temperatures.

### 3. APPLICATION OF LIMA TO JFTOT TUBE DEPOSIT ANALYSIS

LIMA analysis of the deposits has shown variations in the chemical composition with respect to temperature and tube location. The proportion of aromatic to aliphatic hydrocarbons is seen to increase towards the maximum tube temperature and also nearer the tube surface in a deposit, where presumably a temperature gradient exists across the deposit. As such, it may be that chemical changes occur in the deposit after it has been laid down and that therefore characterisation of the deposit in this way may not be a fruitful exercise.

#### 3.1 MDA studies

The presence of MDA on tube surfaces has been shown by LIMA. The negative ion spectrum generated from analysis of MDA on stainless steel or aluminium substrates shows characteristic peaks at 119 and 146 amu (atomic mass units) (Fig 9). These peaks have been observed in spectra from tubes which have been contacted with dodecane or fuel containing MDA, at ambient or at elevated temperatures (Fig 10). They have not been observed during analyses of new JFTOT tubes or deposits generated from fuels which had not been treated with MDA, when peaks characteristic of fuel degradation products only are observed.

Immersion of a new JFTOT tube in fuel containing MDA at ambient temperature results in a layer of MDA on the tube surface, identifiable by LIMA. Variation in contact time does not appear to alter the level of coating, although absolute levels of MDA were not quantifiable. These tests are confirmation of the affinity of MDA for virgin metal of the JFTOT tube surface. The "strength" of the MDA coating can be demonstrated by performing tests on tubes pre-coated with MDA by immersion in treated fuel; the MDA is not removed in subsequent JFTOT tests using untreated fuel. There is however, some evidence for carryover of MDA from previous JFTOT tests although the extent of carryover is insufficient to have a measurable influence on visual rating or TDR assessments.

The passivation role attributed to MDA in the JFTOT test is undoubtedly related to the affinity of the additive for the metal surface. LIMA provides the opportunity to study the phenomenon in detail.

#### 4. FORMATION OF PARTICULATE MATERIAL DURING THERMAL STRESSING

Tests on the modified HLPS have shown that in addition to tube deposition, substantial filterable deposits are formed which are not normally detected in standard JFTOT tests, and at temperatures below the recognised breakpoint of the fuel. These increase exponentially with temperature (Fig 11).

The influence of fuel metal content was demonstrated by addition of copper and iron (as naphthenate) to the fuel, when there was a significant increase in the mass of deposit at a given temperature (Figs 12, 13). With copper, the level of tube and filterable deposits increased with fuel copper content and copper was observed to be inherent in the deposits in increasing amounts. In contrast, while iron had a detrimental effect, there appeared to be a limiting level of iron above which formation of filterable deposits was not increased. Also, iron was not present in the tube deposits, but was observed in the filter deposits. These data coupled with results from other JFTOT studies (Section 2.4) suggest that the deleterious effects of iron and copper are caused by different mechanisms. In particular, iron appears to behave as a catalyst and is not inherently involved in deposit formation on the tube, whereas copper appears to combine with fuel species to promote deposition, in addition to any catalytic role it may have.

Addition of excess MDA to the metal doped fuels restored the quality to that of the base fuel (Figs 12, 13) indicating that the MDA was effective in negating the effect of the metals. To what extent this was caused by passivation of the tube surface and hence reduced reactivity, or by a genuine bulk fuel improvement is at this stage unclear.

The rate of formation of filterable deposits is shown in Fig 14. Initially, there was a linear increase, but thereafter, the rate of formation was reduced. (The fuel flow rate is kept constant throughout the test by adjusting the variable speed pump to compensate for the increase in pressure differential across the test filter.) It is proposed that the rate of formation of filterable deposits is affected by two factors. As deposition occurs on the tube surface, (i) the surface reactivity of the tube is inhibited, leading to reduced overall fuel degradation, and (ii), the tube exhibits enhanced adhesion properties, such that bulk fuel degradation products are retained, leading to an increase in tube deposition and a decrease in filterable deposits. This is shown schematically (Fig 14) where the tube deposits have been calculated as the difference between linearly increasing filterable deposits and actual measured levels. The variation in tube deposits with time is in good agreement with SEM/EDX data generated from JFTOT deposits (Section 2.3). Also, the mass of tube deposits predicted is of the same order of magnitude as measured by others in carbon burn-off assessment of JFTOT tube deposits (3).

Particle size measurements performed using laser diffraction techniques (Fig 15) demonstrate large increases in the number of particulates after thermal stressing, with the majority in the sub-micron size range. The implications for aircraft fuel system operation need to be established.

#### 5. CONCLUSIONS

SEM/EDX and LIMA have been used for reliable characterisation of JFTOT and HLPS tube deposits providing information about deposit formation in relation to operating parameters and fuel composition. Tentative mechanisms for the role of metals and MDA on thermal stability have been proposed.

Tests on a modified HLPS have shown that substantial filterable deposits are formed during thermal stressing of fuels which are not detected in standard JFTOT tests. These have been shown to occur at temperatures below the JFTOT breakpoint of the fuel and to vary with temperature and fuel composition. Models have been proposed to demonstrate the relationship between tube and filterable deposits. These initial investigations will form the basis for more detailed studies on jet fuel thermal stability.

## 6. REFERENCES

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## 7. ACKNOWLEDGEMENTS

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TABLE 1

JFTOT DATA OBTAINED ON MEROX TREATED KEROSENE SHOWING THE EFFECTS OF METALS AND MDA ON TUBE RATING

FUEL			Temp °C	TDR			PRESSURE Δ p-mmHg	VISUAL RATING	MAXIMUM C/A1 RATIO
Cu (ppb)	Fe (ppb)	MDA (ppm)		Spun	Spot	Posn			
-	-	-	260	2.5	3.5	45	0.1	<2	0.08
83	-	-	260	14	15	44	0.2	4	0.74
166	-	-	260	16	17.5	31/49	0.3	4	1.36
83	-	5.70	305	5.5	8.5	44	>25	A	0.38
83	-	0.57	260	0	0	-	0.2	1	0.03
83	-	0.57	305	50	50	38	2.5	>4	2.50(9kv)
-	-	0.57	305	9	11	43	0.7	2A	ND
-	-	1.14	305	0	0	-	0.3	1	ND
-	-	2.28	305	0	0	-	0.4	1	ND
-	78	-	260	44	45	38	>25	4	10.1(5kv)
-	78	5.7	260	0	0	-	3.3	1	ND
-	78	5.7	305	22	25	42	>25	4P	0.64(5kv)

ND - Not Determined

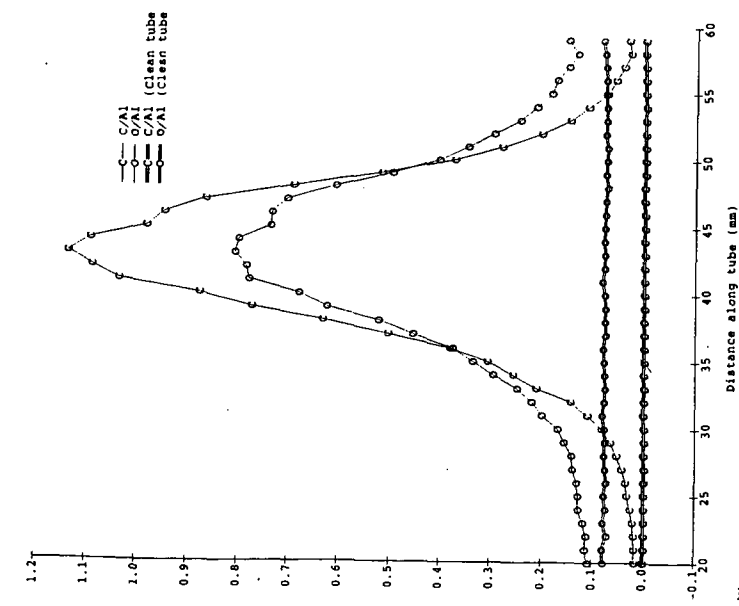


Figure 1. Typical SEM / EDX profile for JFTOT deposit with result from clean tube for comparison.

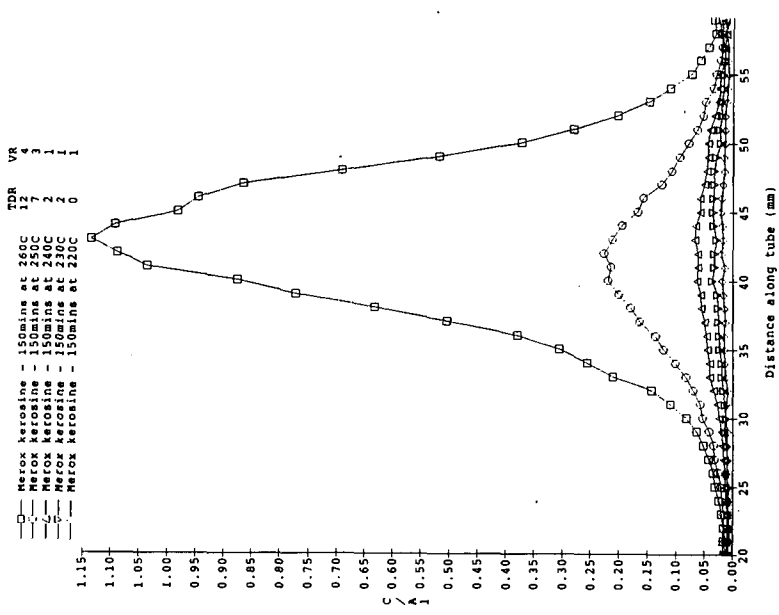


Figure 2. Carbon deposition on JFTOT tubes: Correlation with TDR and VR.

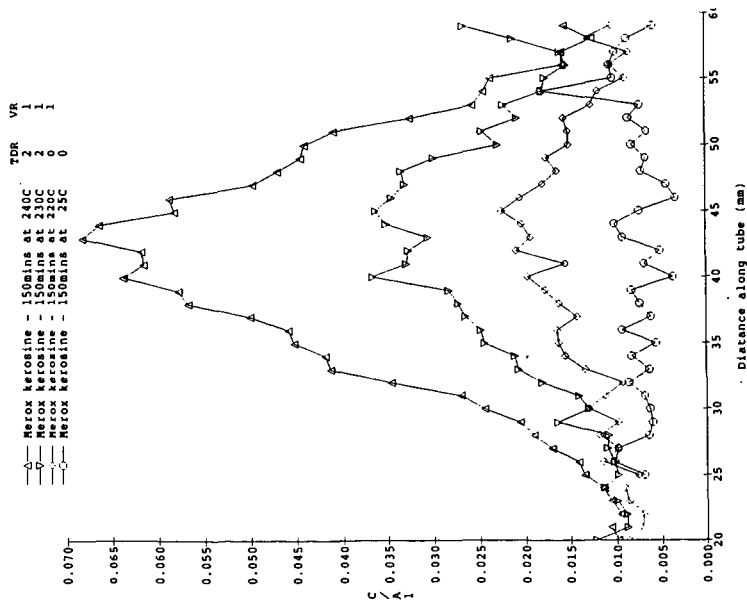


Figure 3. Carbon deposition on JFTOT tubes: Correlation with TDR and VR.

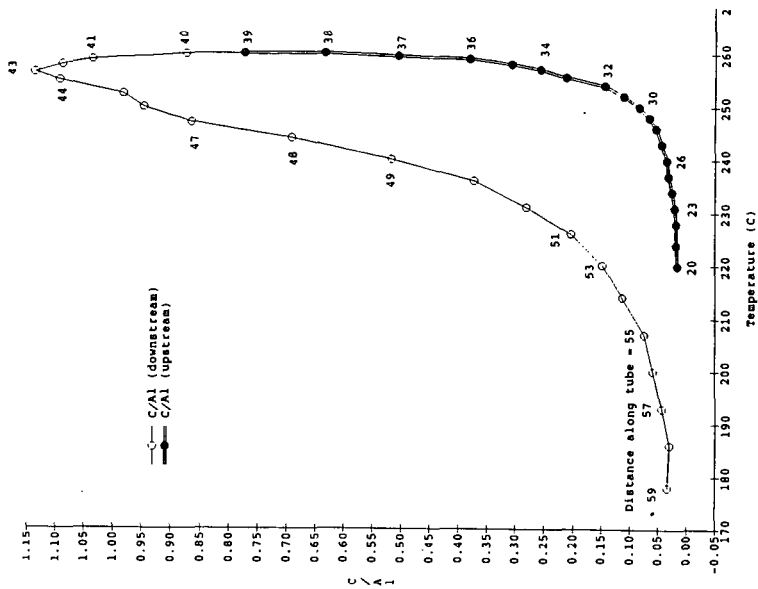


Figure 4. Temperature profile of carbon deposit Merox kerosene at 260°C.



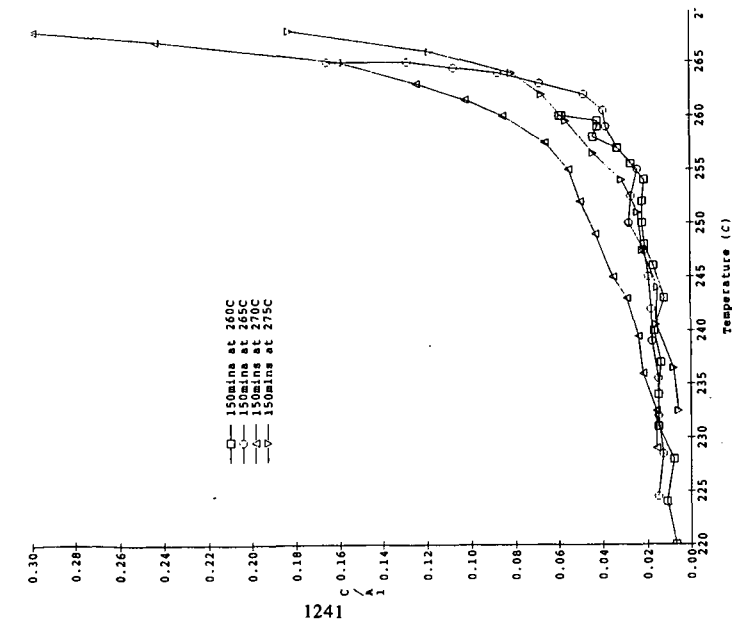


Figure 5. Relationship of upstream C / Al ratios to temperature of deposition (Merox kerosine).

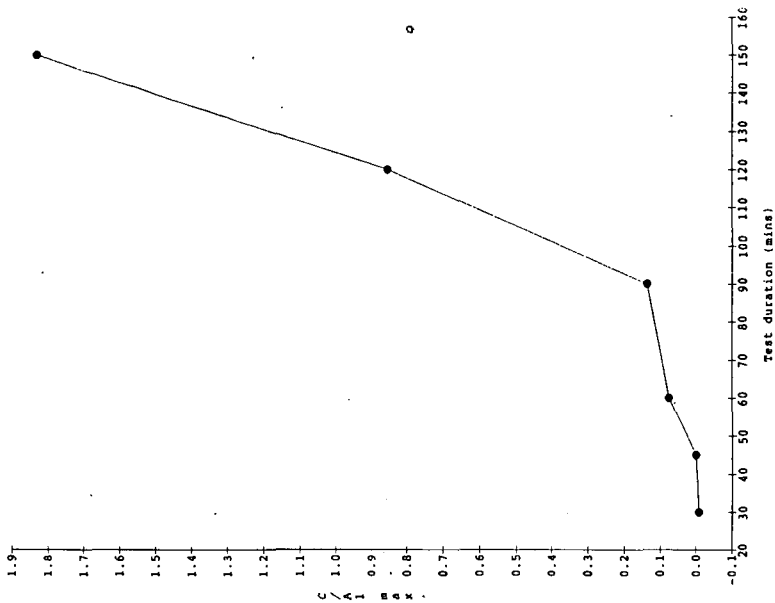


Figure 6. Maximum C / Al ratios against test duration -Merox kerosine at 275°C.

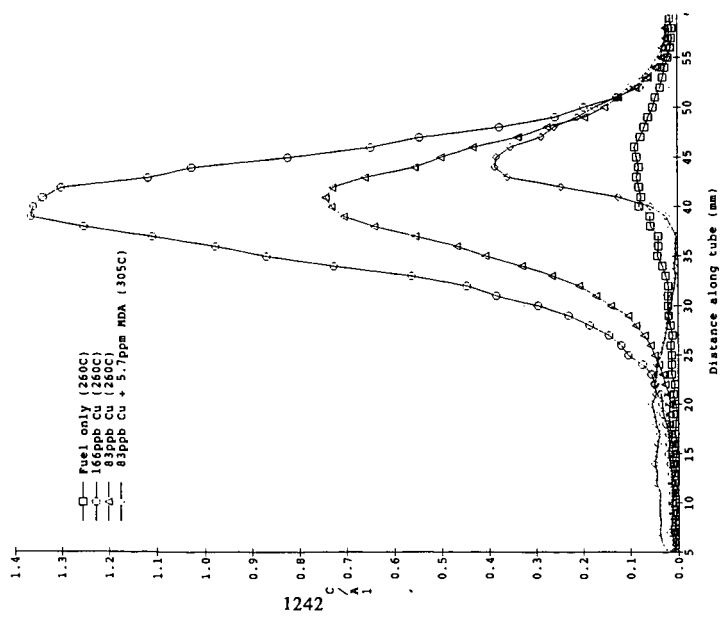


Figure 7. Comparison of C / AI ratios for Merox kerosene blends.

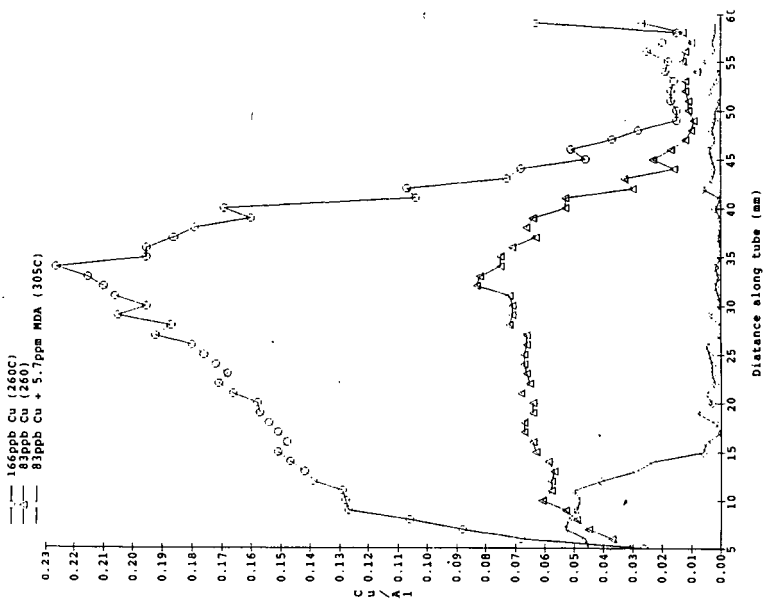
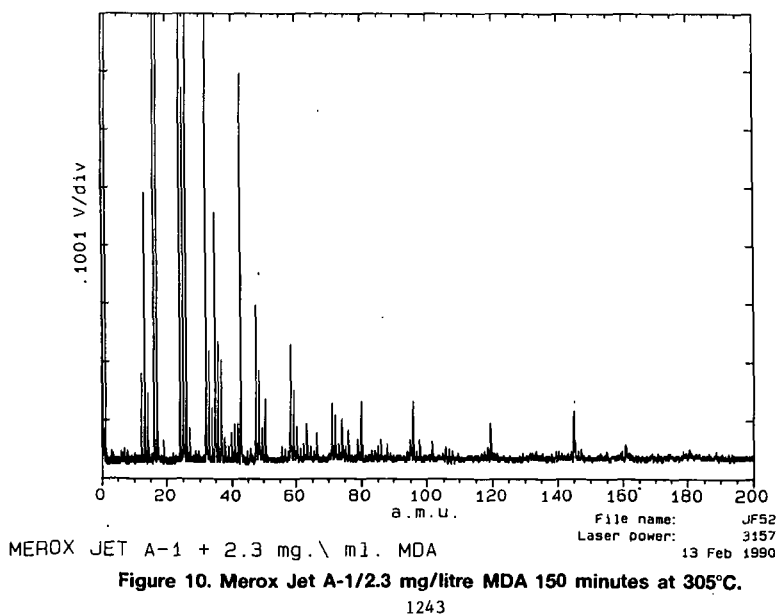
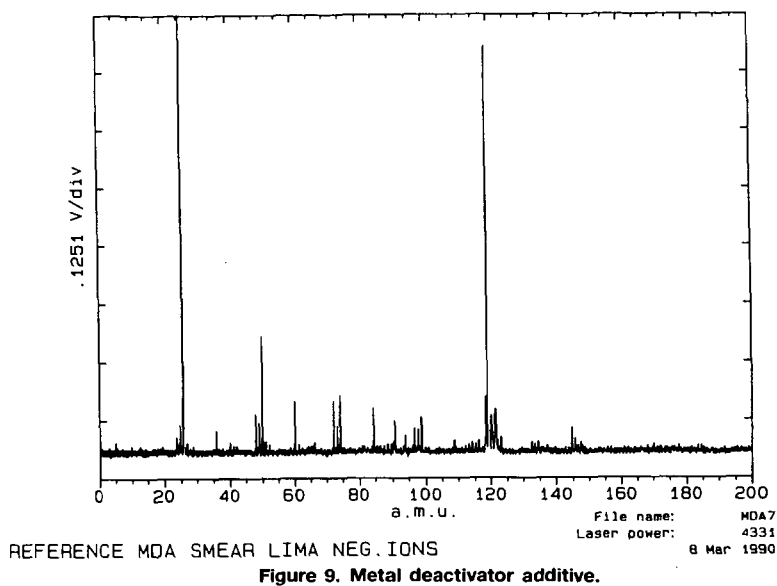


Figure 8. Comparison of Cu / AI ratios for Merox kerosene blends.



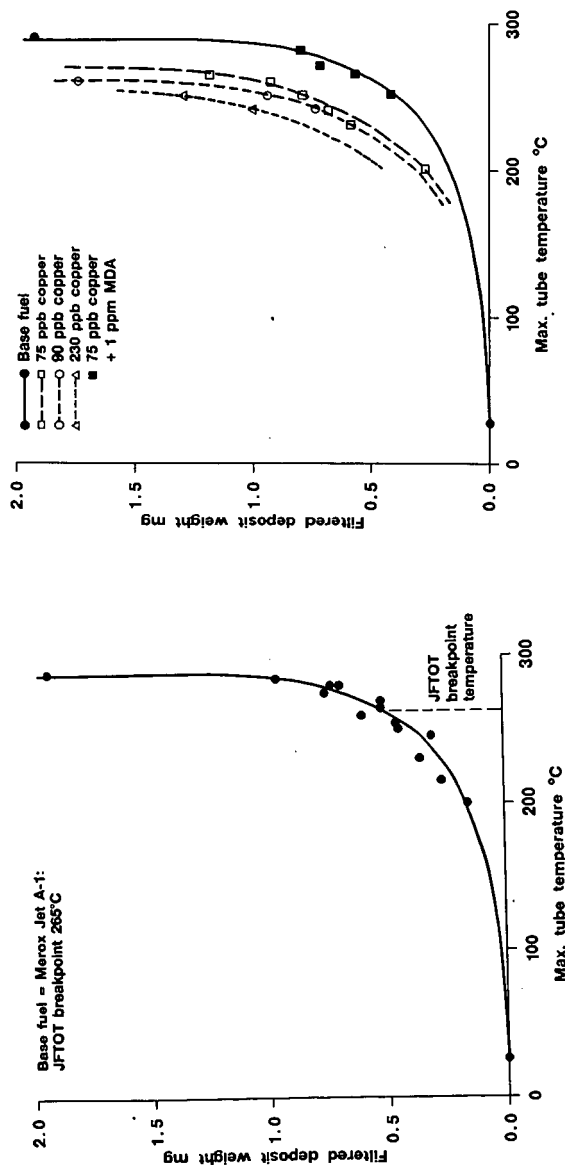


Figure 11. Modified HLPS tests. Influence of temperature on filtered deposit levels.

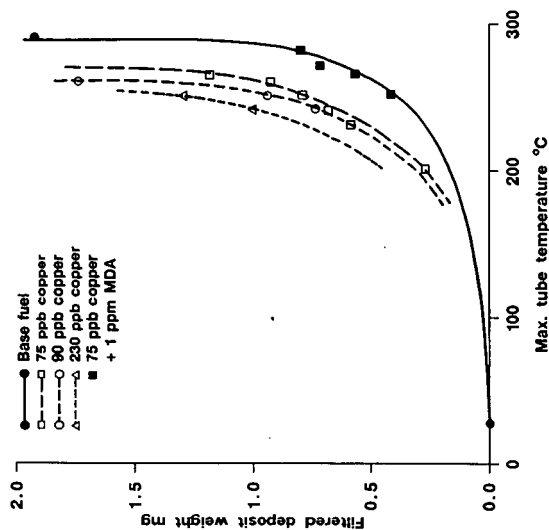


Figure 12. Modified HLPS tests. Influence of soluble copper and MDA on filtered deposit levels.

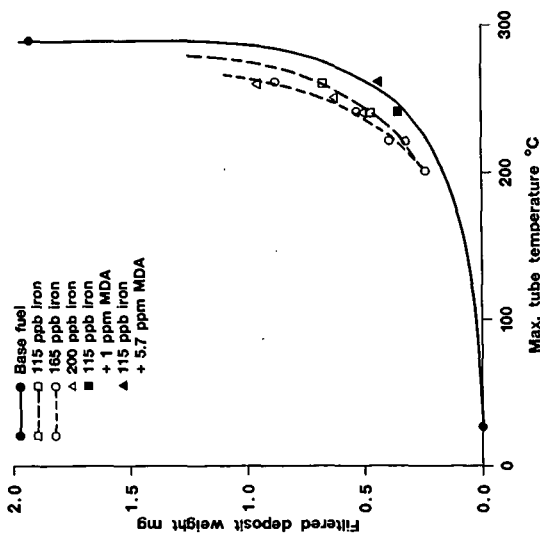


Figure 13. Modified HLPS tests. Influence of soluble iron and MDA on filtered deposit levels.

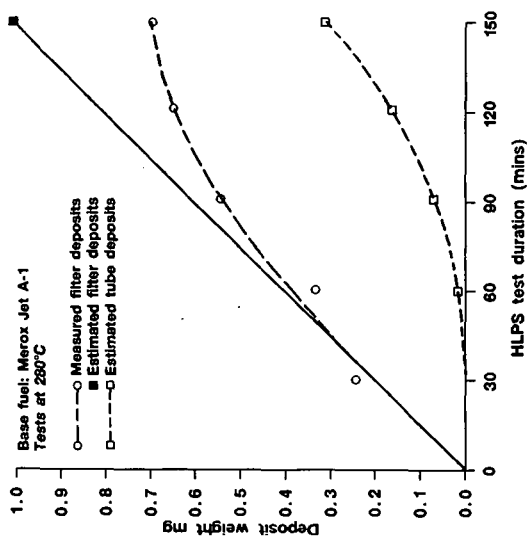


Figure 14. Modified HLPS tests. Relationship between tube and filter deposits.

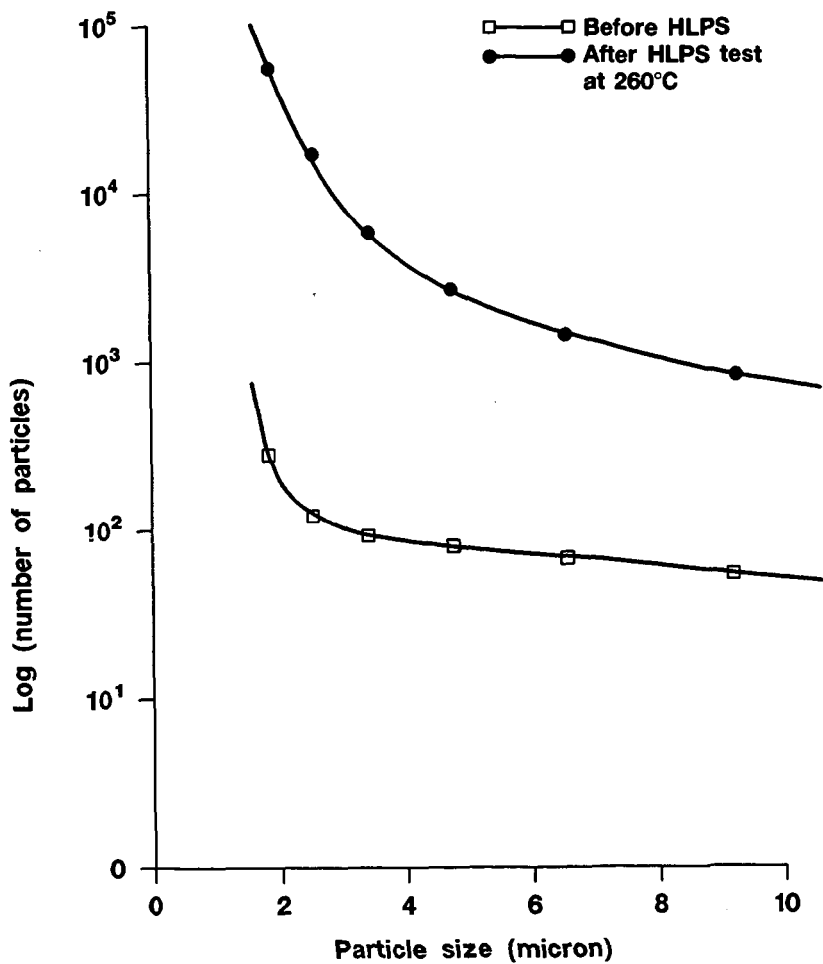


Figure 15. Influence of thermal stressing on particle size (number) distribution. Fuel: Merox Jet A-1 + 75 ppb copper.